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ENVIRONMENTAL SCIENCE FOR THE EUROPEAN REFINING INDUSTRY

Dermal exposure assessments for REACH dossiers of Petroleum Substances

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Main reasons for studies

- Heavy Fuel Oil (workers): proven toxic including CMR effects via the dermal route in animals – very low DNEL for dermal exposure:
  - Expected difficult to prove 'safety' based on conservative, simplistic models
- Consumer handling of diesel fuel and lubricants: DNELs for consumers lower than DNELs for workers
  - Direct studies on consumers not practicable, therefore used panel of volunteers to simulate exposures
- Diesel fuel, service station attendants (workers): initial exposure estimates > DNEL, had to assume use of gloves in REACH dossier of 2010 to prove 'safety'
  - But attendants in the main do not wear gloves
  - Contaminated gloves not acceptable for customer-facing staff

Heavy Fuel Oil study - overview

Conducted before DNELs were known (anticipated to be low, but even lower when established)

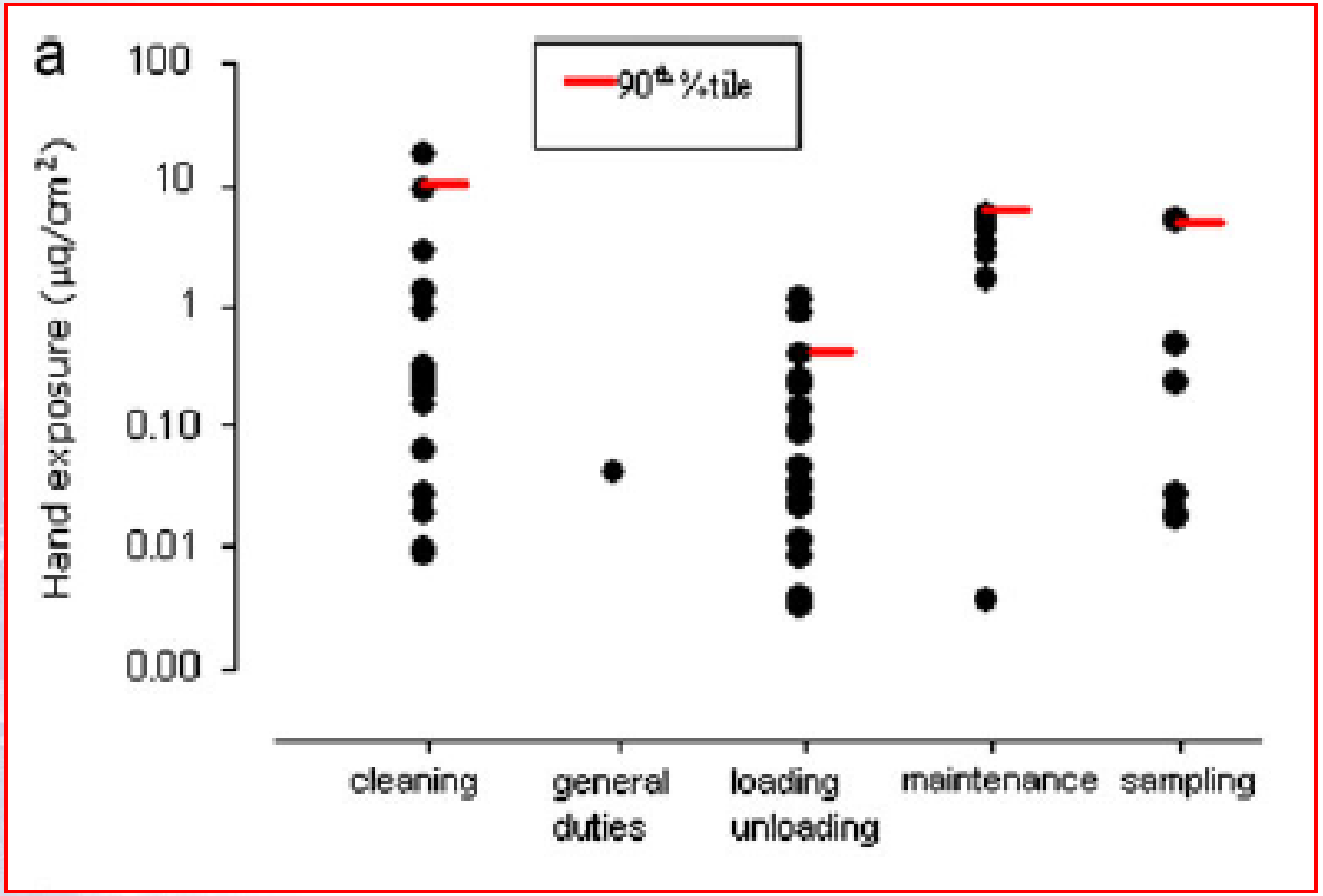
Study took ~2 years, >100K € to sample some 60 workers

- Workplaces and worker tasks studied
  - Refineries: line spading, filter cleaning, product sampling, heat exchanger tubes cleaning
  - Distribution terminals: pump maintenance, ship and truck loading, product sampling
  - Power plant: product unloading, pump maintenance, filter and spillage cleaning, tank dipping
  - Marine engine repair facility: cleaning injector nozzles, drip trays, filter cleaning and changing
  - Almost all workers wore leather or PVC gloves
  - Note: HFO usually at elevated temperature which would cause skin burns
- Developed novel exposure sampling and analytical techniques
  - Wipe sampling of hands, forearms and neck

Heavy Fuel Oil study – main results

- General: HFO was detected in 60% of hand wipe samples
  - And in ~20% of the samples from forearms
  - But only 3% of neck samples
- General: Detected levels on hands were ~10x higher than on forearms
- Industry with highest exposure levels was marine engine repair, followed by distribution terminals
- Worker activities with highest exposure levels were cleaning and maintenance, followed by product sampling
  - No glove use in maintenance involving fine repair work due to dexterity issue – could be overcome with special thin gloves

Heavy Fuel Oil study – main results



Heavy Fuel Oil study – Concluding remarks

- Study execution was challenging, expensive and time consuming
  - >1000 € per sampled worker
- Limited but very informative data set obtained
  - Very good sensitivity by using PAH trace analytical technique
- Exposure levels (much) lower than predicted by simplistic ECHA recommended Tier-1 models – so study was worth doing
  - Able to show that these levels were below the dermal DNEL for HFO
  - > 4 orders of magnitude difference in some data set for a given task
  - High temperature of bulk product will also cause avoidance of contact
    - Studies with e.g. Metal-working fluids show much higher levels
- Gloves reduce exposure, but do not prevent it
- N.B.: Due to the classification as CMR, all exposures to HFO need to be managed to levels as low as reasonably practicable

Determination of potential for dermal exposure from transfer of lubricants and fuel by consumers

- **CONSUMERS**

IOM

Exposure situations and products to be assessed

Four Exposure situations were assessed in the study:

1. Filling a fuel tank with **diesel**
2. Filling an engine with **lubricating oil** (easy)
3. Filling an engine with **lubricating oil** (filling point more difficult to reach, hard)
4. Lubricating a bicycle chain with **cycle oil**

Approach Taken

- Ten volunteers completed a series of exposure situations to simulate the activities for a total of 80 experimental runs (20 for each operation).

- Dermal exposure was assessed using
  - a validated **wipe sampling** method
  - the products' natural fluorescence under ultra-violet (UV) light.
  - the DREAM methodology
  - Covering the hands, forearms and spills

Approach Taken

- The filling practices of participants were observed and filmed to ensure that key 'exposure defining' events were captured

Table 16 Number of tests where spills and contamination were recorded to have occurred. Also the number of tests where low, medium and high care were taken and the volunteers complied fully with the instructions.

Situation	Spills	Contaminated	Compliance	Care - L	Care - M	Care - H
ES1 Diesel	13	10	20	1	2	17
ES2 Easy	8	9	20	2	9	9
ES3 Hard	12	5	20	5	8	7
ES4 Bike	18	8	15	1	3	16

L-low; M-medium; H-high

- An estimate was made during each test of the amount of product spilled
- The reasons for contamination varied between the exposure situations.

Table 17 Estimated quantity (ml) spilled during the tests, by exposure situation.

Quantity Spilled (ml)	ES1 Diesel	ES2 Easy	ES3 Hard	ES4 Bike
0	7	12	8	2
<20	5	8	9	17
20-50	1	0	3	1
50-200	3	0	0	0
200-500	2	0	0	0
>500	2	0	0	0

WIPE SAMPLES RESULTS

- Wipes were taken pre- and post test on each hand and forearm
- The measured mass was provided in mg and converted in μg/cm2 using average surface area for forearm and hands

Table 22 Summary of the levels (μg/cm^2) measured at post test for dominant and non-dominant hand shown separately for whether spills were recorded to have occurred or not.

Hand	Spill? (N)	AM	GM	GSD	MIN	MAX	90th %
Dominant	No (7)	17.66	2.12	10.93	0.25	96.21	81.05
	Yes (13)	19.16	3.01	11.27	0.25	76.06	73.47
Non-Dominant	No (7)	5.91	2.29	4.08	0.25	30.13	24.71
	Yes (13)	5.74	1.26	6.08	0.25	40.62	20.41

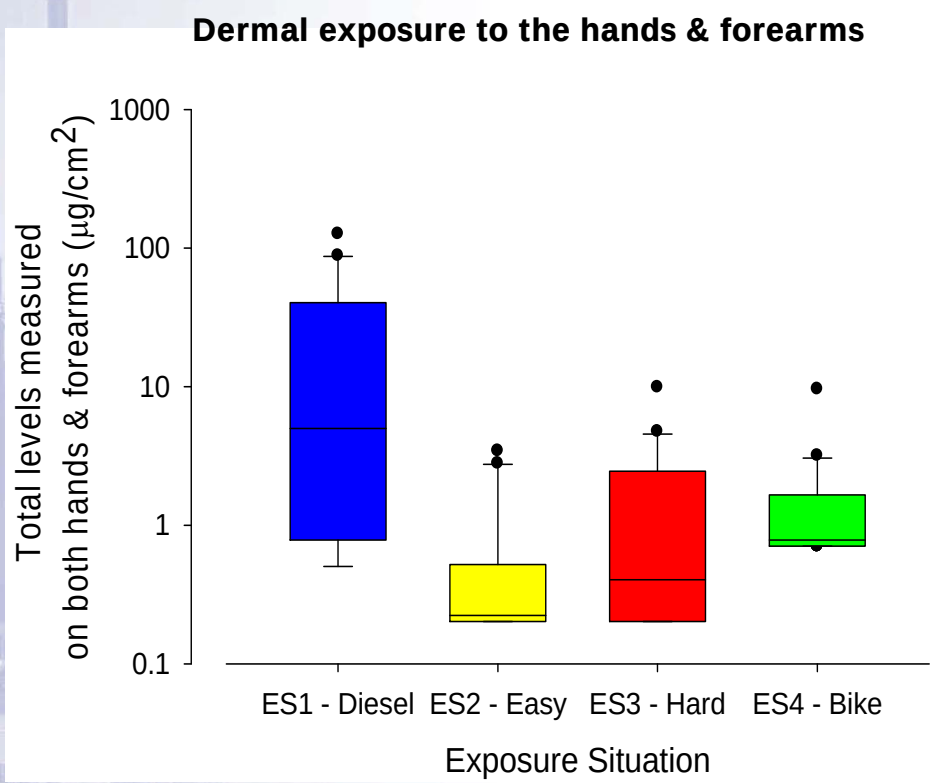
•Significantly higher dermal exposure was observed when a lower level of care was taken to complete the task.

•the within volunteer variation was relatively large (likely due to the few high measurements)

WIPE SAMPLES RESULTS

- A high proportion of samples was less than the limit of detection (ES1=38%, ES3=60%, ES2 and 4, both 78%).
- In ES2 Easy and ES3 Hard, the hand and forearm results ranged from <0.1 µg/cm(2) to 3.33 µg/cm(2) and from <0.1 µg/cm(2) to 3.54 µg/cm(2), respectively.
- In ES4 Bike, the hand and forearm exposures ranged from <0.35 µg/cm(2) to 5.25 µg/cm(2).
- Not all volunteers fully complied with the ES4 instructions, thus highlighting that this situation may have more variability in consumer behaviour.

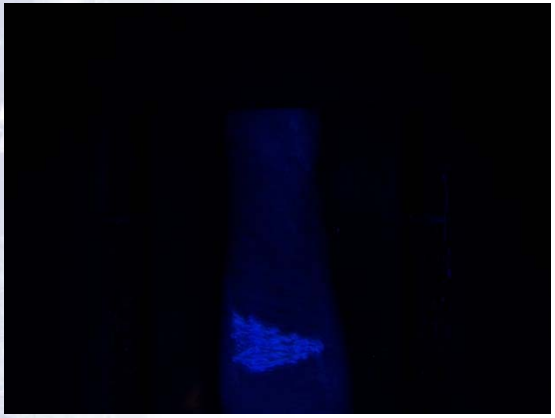
Results : Dermal Transfer



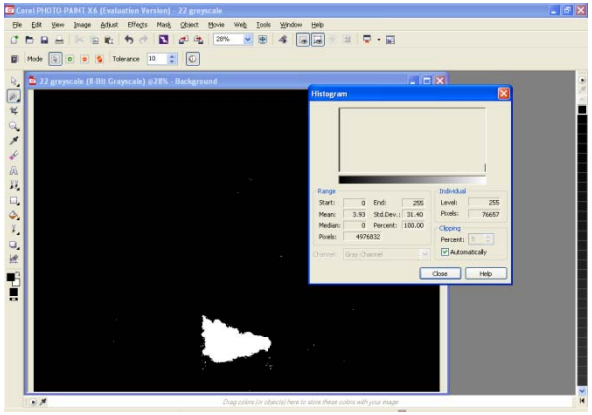
- The ratio of the total amount measured on the hands & forearms to the amount handled for ES1, 2 and 3 was less than 0.0001% whereas ES4 was 0.04%.
- There was no direct relationship between the amount handled and that measured in the wipe samples.
- For ES2, 3 and 4 both between and within volunteer variation was small.
- For ES1-diesel, the within volunteer variation was relatively large, likely due to the few very high values.

Results : Fluorescence

- As an alternative assessment of dermal exposure it was proposed that digital images of each hand (dorsal and palmar regions) and forearm would be collected under UV light in a light tight box prior to the individual completing the exposure scenario.
- Whole body images (front and back) were also be captured in a blackened out room.
- Sensitivity of fluorescent UV method only enables a qualitative assessment of dermal contact
  - Affected body locations and 'intensity' of the contamination
  - Method shown to have potential utility especially if baseline sensitivity improved via use of synthetic UV tracers (BUT issues relating to subsequent decontamination of affected equipment)



Post exposure image of left forearm under UV light



Number of pixels fluorescing compared with pre-exposure image

Preliminary evaluation of the dermal exposures associated with service station refuelling activities

- **WORKERS**

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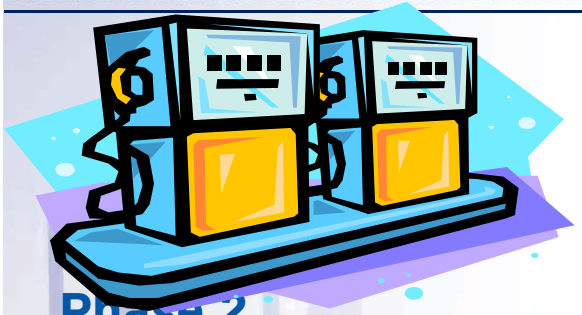
APPROACH TAKEN: monitoring strategy



Phase 2

Evaluation of the **dermal transfer coefficient** from equipment surfaces to skin

Wipe samples -3 days, samples taken every hour 1 Station 1 attendant

Phase 1

1. **Quantification of hydrocarbon levels on hands** of attendants at the end of the work shift,
2. Quantification on nozzle grip, button panel, dispenser hoses,
3. **protective capacity of the clothing** worn

Washing of two hands and surfaces wipes for 3 days on 3 stations, 6 attendants

Questionnaires were given to the attendants in order to evaluate factors that may have altered results (use of hand cream, clothing..)
Other data were recorded: Type of service station, amount of fuel dispensed,…

APPROACH TAKEN: : monitoring strategy

Dermal Exposure techniques: based on three sampling approaches:

- **Removal** : Wipe , hand washing removal of the contaminant from the skin by applying an external force equal to or greater than the force of adhesion of the contaminant to the skin by washing or wiping the surface
- **Interception**: patches – It intercepts the mass transport of the hydrocarbon by collecting the sample onto a medium (cutaneous surrogate) placed on the skin surface or on the clothing .

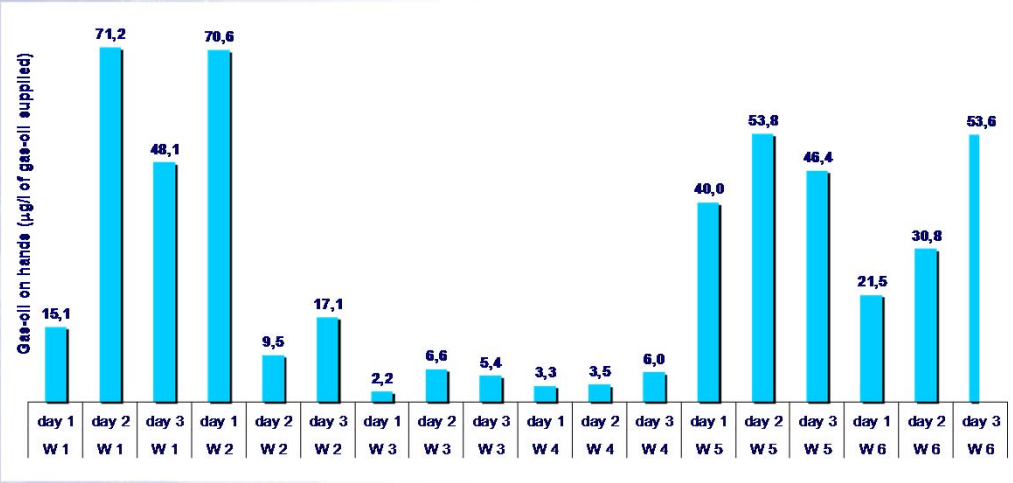
- **Surface sampling:** valid for hydrocarbon transfer from direct skin contact with a contaminated hard surface .Involves sampling the residual hydrocarbon on the surface in order to make an indirect inference regarding the dermal load (dermal transfer coefficient (DTC))

Results: **HAND WASHING**

Hand Washing: 18 samples

High Variability:

- workers operate outdoors and are in contact with different surfaces which show different levels of residual products
- Different number of refuelling operations
- Removal of product due to Dermal transfer to other surfaces, evaporation or other factors



The **measured exposures on hands were found to be much lower (worst case less than 1/5th)** than the estimates predicted using exposure modelling tools such as ECETOC TRAv.2

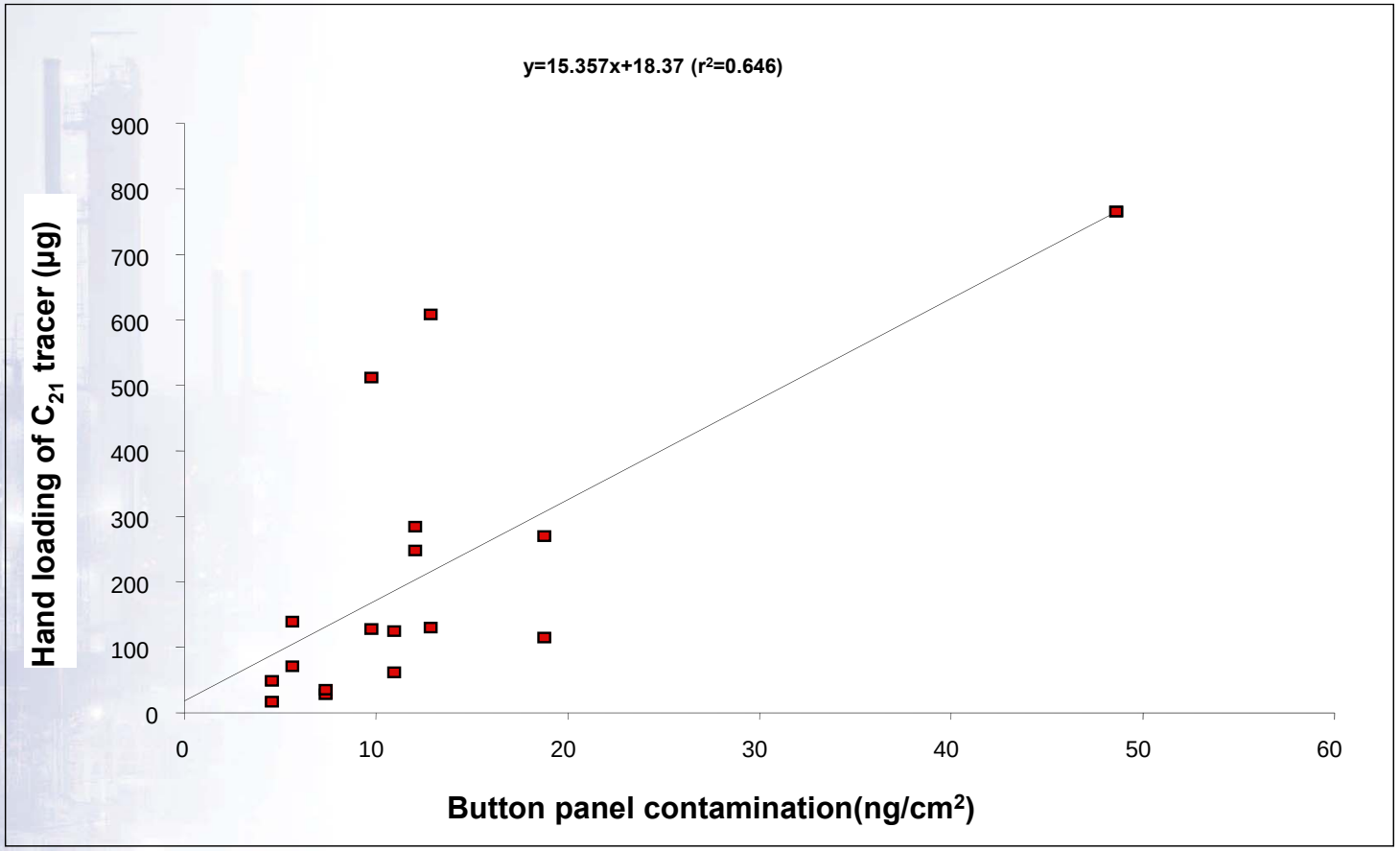
RESULTS – PAD and WIPES

PADS: PROTECTIVE CAPACITY OF CLOTHING

- Measurement of hydrocarbon levels inside and outside the clothing in the same skin area to determine the protective capacity of the clothing worn: cotton work clothing may reduce hydrocarbon vapor concentrations 15%-60% but not from contact form liquid

- WIPES: DERMAL TRANSFER FACTOR (DTF)
- Ratio between the amount on hands (ng/h), and the average concentration on surfaces (ng/cm2) (pump nozzle grip and button panels), assessed every hour

Results wipes and hand washing: **levels of petroleum hydrocarbons on equipment**



Linear regression analysis comparing C_{21} contamination on the button panel with loading onto the hands

CONCLUSIONS

1° study: CONSUMERS exposure – Products: Diesel, Lubicants

Test environment with volunteers – single operation

2° Study: WORKER exposure – Products: Diesel, Gasoline

Real life environment with workers – whole shift (phase 1)
hourly samples (phase 2)

A preliminary analysis of the two studies shows:

- When workers exposure for a whole shift is divided into one single refuelling operation the result is much lower than consumers' exposure
- The gap is reduced when considering lower results
- This difference may be due to: monitoring techniques, Workers' training, absorption , removal of product from hands for whole shift samples
- Measured workers' exposure are much lower than estimates form algorithms
- A detailed exposure assessment is complex for substances like gasoline and diesel and is affected by a lack of a universal validated measurement method

Observations from studies completed so far

- New area of exposure assessment for downstream oil industry – but required under chemical regulations
- Studies provide 'Tier-2 data' that can override (grossly) conservative Tier-1 estimates
  - But data sets are small, may not be 'representative for the EU'
  - Expensive, labour-intensive, large variability

Conclusions & Next Steps

- Lack of standardisation of methods and sampling strategies
  - Nature of Petroleum Substances also of relevance (e.g. High viscosity products are handled hot; volatile substances evaporate from skin)
- Exposure pathways can be complex, e.g. button on pump contaminated by hand
- Include in REACH dossiers as 'supporting data' or first obtain larger data sets?